Analysis of the Lennard-Jones-38 stochastic network

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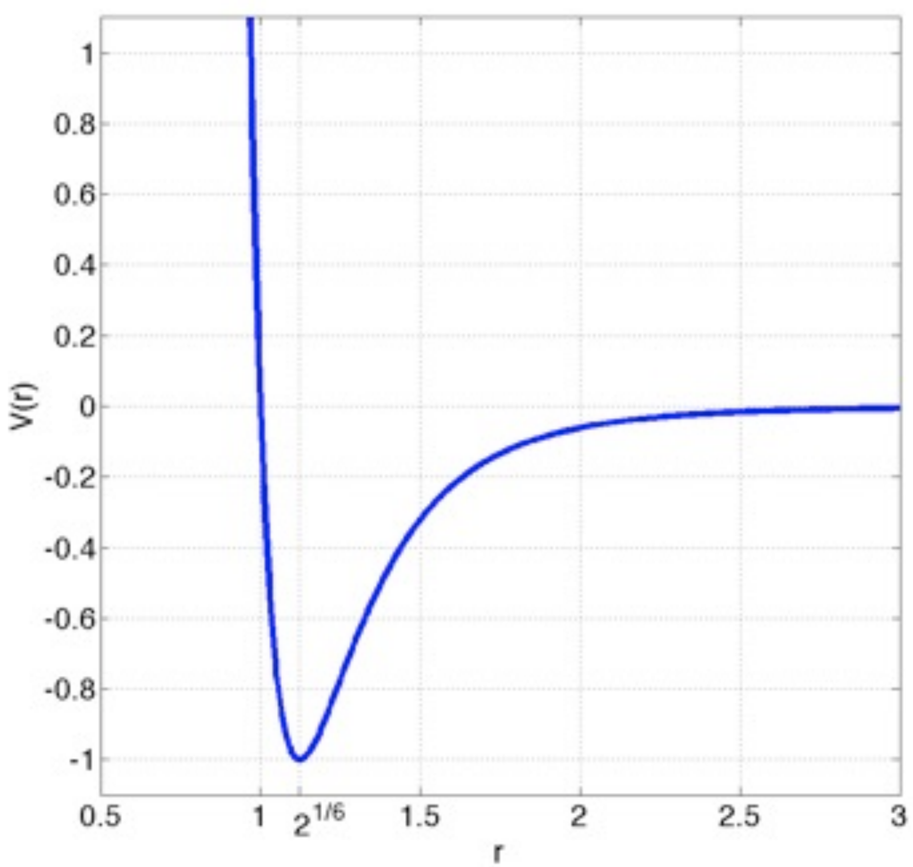
Joint work with E. Vanden-Eijnden

Lennard-Jones clusters

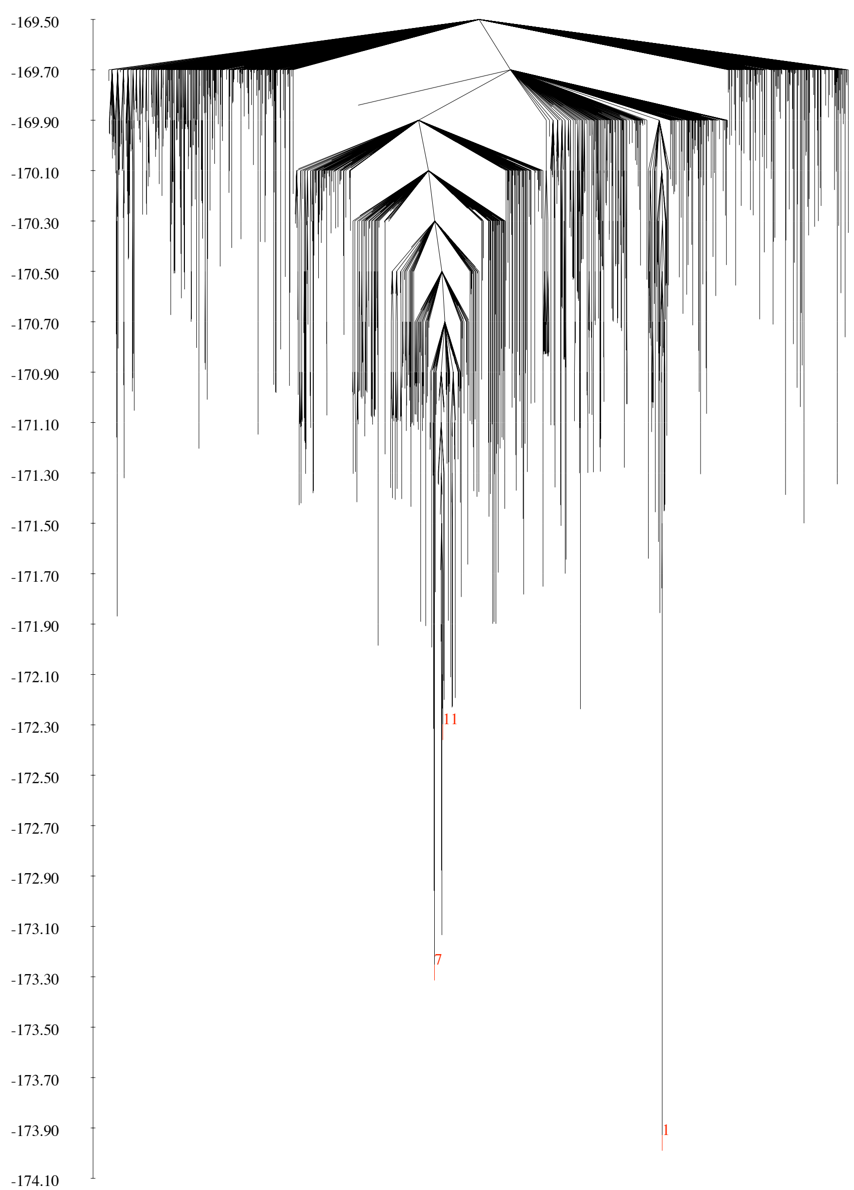
Pair potential: $V(r) = 4e(r^{-12} - r^{-6})$



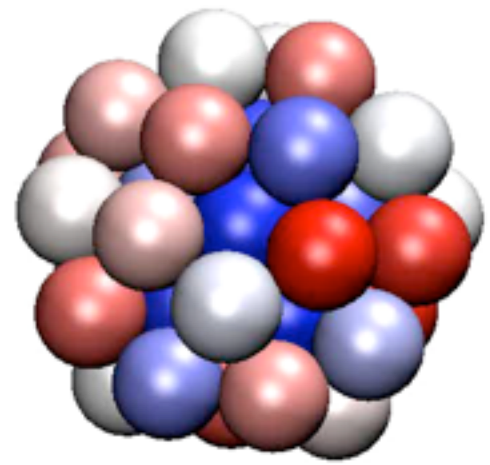
1. Wales, D. J., Energy landscapes: calculating pathways and rates, International Review in Chemical Physics, 25, 1-2, 237-282 (2006)
2. Wales's D. J. website contains the database for the Lennard-Jones-38 cluster: http://www-wales.ch.cam.ac.uk/examples/PATHSAMPLE/
3. Wales, D. J. and Doye, J. P. K. Global Optimization by Basin-Hopping and the Lowest Energy Structures of Lennard-Jones Clusters containing up to 110 Atoms. J. Phys. Chem. A 101, 5111–5116 (1997)
4. Doye, J. P. K., Miller, M. A. and Wales, D. J. The double-funnel energy landscape of the 38-atom Lennard-Jones cluster. J. Chem. Phys. 110, 6896–6906, (1999)

D. Wales's LJ_{38} network

Double-funnel of LJ38

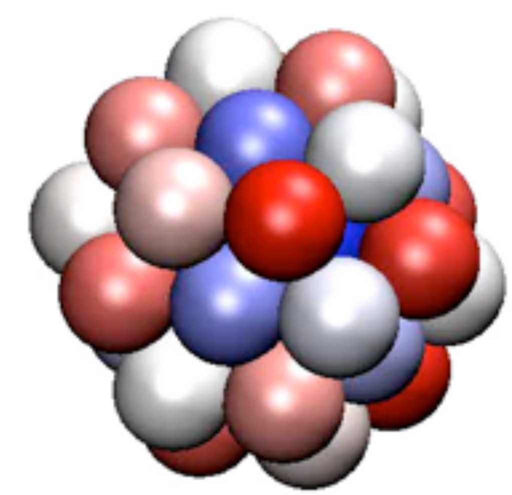


100000 minima
138888 transition states



The second lowest minimum:
incomplete icosahedron
point group C_{5v}

The lowest minimum:
face-centered cubic
truncated octahedron,
point group O_h



Critical temperatures

Mandelshtam,V.A.and Frantsuzov,P.A.,

Multiple structural transformations in Lennard - Jones clusters: Generic versus size-specific behavior,

J. Chem. Phys. 124, 204511 (2006)

- $T = 0.12\ e/k_B$ - solid-solid transition when the FCC structures give place to icosahedral packing
- $T = 0.18\ e/k_B$ - the outer layer melts while the core remains solid
- $T = 0.35\ e/k_B$ - the cluster melts completely

Goals

- Analysis of the LJ38 network
- Comparison of three approaches
    - the zero temperature asymptotic (the Large Deviation theory)
    - the discrete Transition Path Theory
    - a heuristic approach

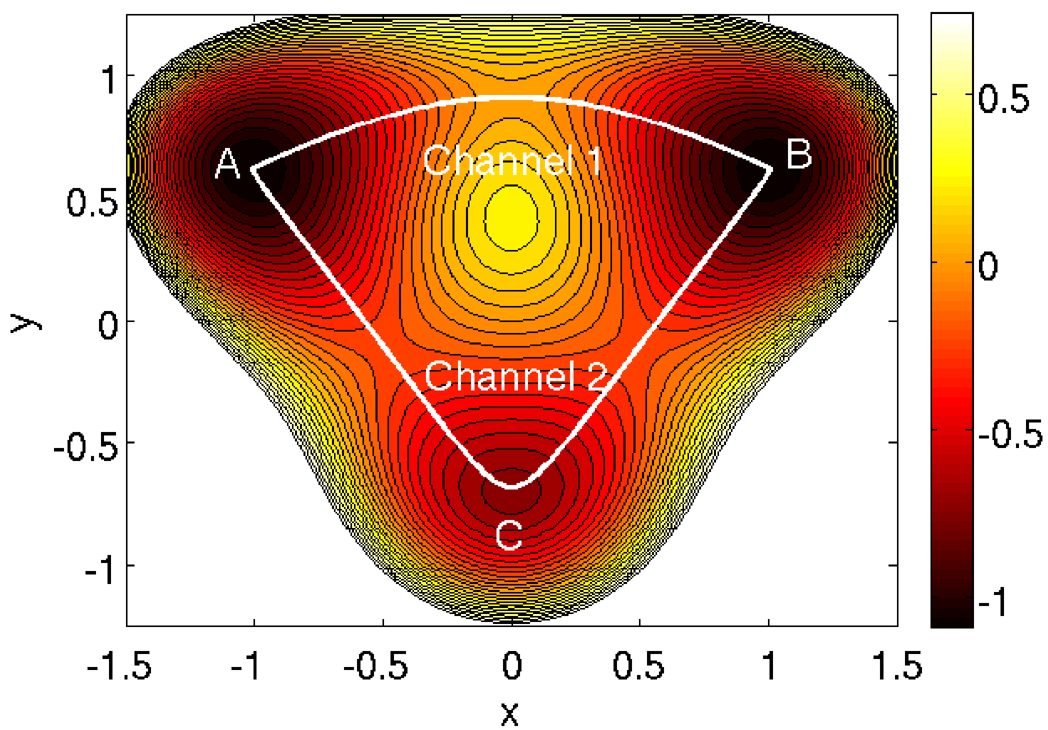
New developments

- Computational algorithm for
    - finding the zero-temperature asymptotic path
    - building the hierarchy of Freidlin’s cycles

Settings

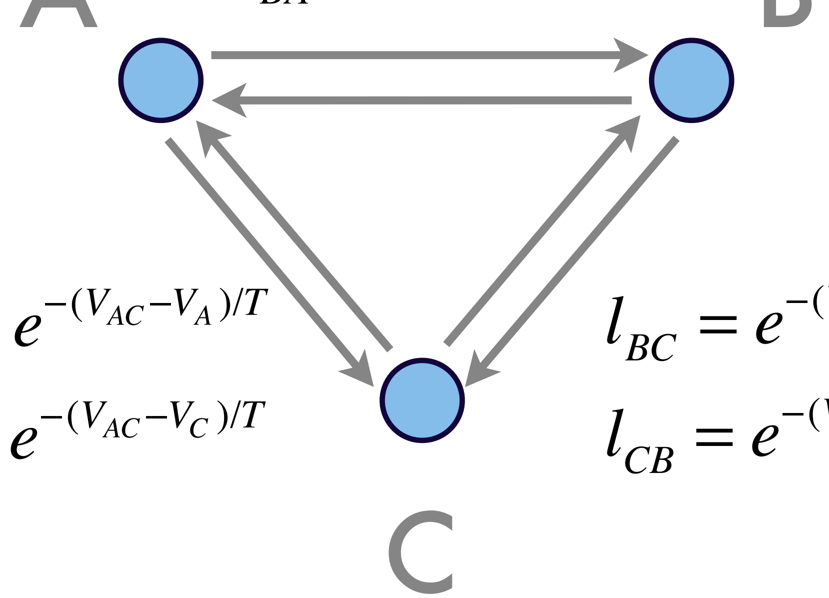
LJ38 network: 100000 minima and 138888 transition states

$$dx = -\nabla V(x)dt + \sqrt{2T}\,dw$$



$$l_{AB} = e^{-(V_{AB}-V_A)/T}$$

$$l_{BA} = e^{-(V_{AB}-V_B)/T}$$



$$l_{AC} = e^{-(V_{AC}-V_A)/T}$$

$$l_{CA} = e^{-(V_{AC}-V_C)/T}$$

$$l_{BC} = e^{-(V_{BC}-V_B)/T}$$

$$l_{CB} = e^{-(V_{BC}-V_C)/T}$$

The generator matrix

$$L_{ij} = l_{ij}, \quad i \neq j,$$

$$L_{ii} = -\sum_{j \neq i} l_{ij}$$

Equilibrium probability distribution

$$\pi_i = \frac{1}{Z} e^{-V_i/T}, \quad i = A, B, C$$

$$Z = \sum_i e^{-V_i/T}$$

Zero-temperature asymptotic

Freidlin (1977): in the case of multiple attractors the system is reduced to a discrete-space continuous-time Markov chain and its dynamics of the system is characterized by the hierarchy of cycles

In the case of gradient system (or a system with detailed balance) the hierarchy of cycles acquires a simple structure:
each cycle (or macrostate) is exited via the lowest saddle adjacent to it.

The zero-temperature asymptotic pathway is defined by the following property: the highest saddle separating any two states along it (not only neighboring) is the lowest possible.
We will refer to it as the minimax pathway.

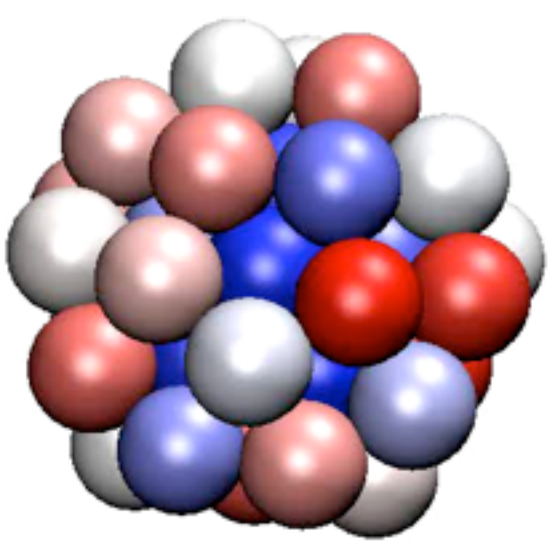
The algorithm for finding the minimax path and building the hierarchy of cycles

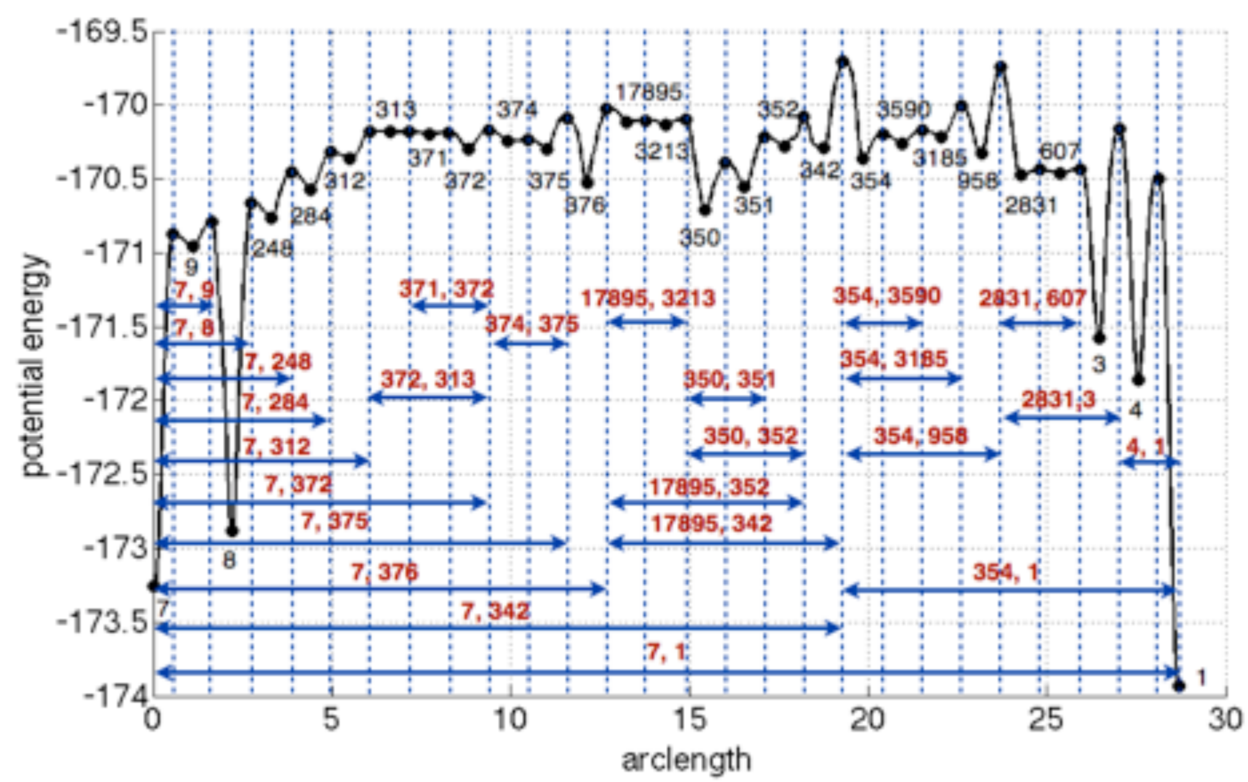
This algorithm recursively builds a tree of minimax edges using, as a building block, the Dijkstra method with

- the cost function $c_{ij} = \begin{cases} V_{ij}, & \text{if } i \text{ and } j \text{ are commected by an edge} \\ \infty, & \text{otherwise} \end{cases}$

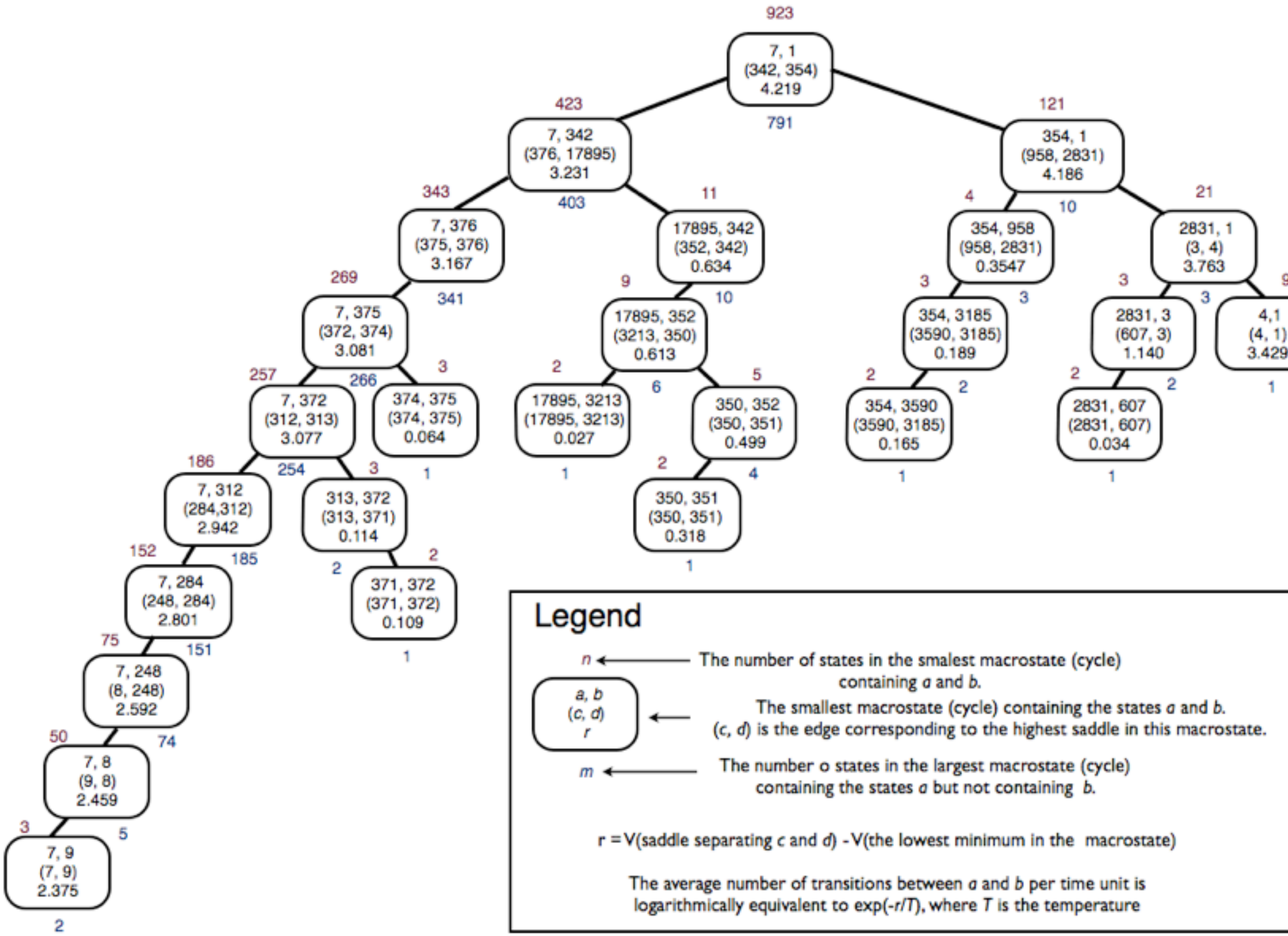
- the value function $u(j) = \min_{w} \max_{(k,l)\in w} V_{kl}$

- and the update rule $u(j) = \min\left\{u(j), \max\left\{u(i), c_{ij}\right\}\right\}$





The hierarchy of cycles and the minimax pathway



The discrete Transition Path Theory

Metzner, P., Schuette, Ch., and Vanden-Eijnden, E.,

Multiscale Model. Simul., 7, 3, 1192-1219 (2008)

Key concepts

- The committor function *q*(*i*) = the probability to reach *B* prior to *A* starting from the state i; it solves

$$\sum_{j\in S} L_{ij} q_j = 0, \qquad i \in S \setminus (A \cup B)$$

$$q_i = 0, \quad i \in A, \qquad q_i = 1, \quad i \in B$$

- The reactive current $f_{ij}^{AB} = \begin{cases} \pi_i (1-q_i) L_{ij} q_j, & i \neq j, \\ 0, & otherwise \end{cases}$

- The effective current $f_{ij}^{+} = \max\left\{ f_{ij}^{AB} - f_{ji}^{AB}, 0 \right\} = \begin{cases} \pi_i L_{ij} (q_j - q_i), & q_j > q_i, \\ 0, & otherwise \end{cases}$

The discrete TPT methodology

- Solve the committor equation

$$\sum_{j\in S} L_{ij} q_j = 0, \qquad i \in S \setminus (A \cup B)$$

$$q_i = 0, \quad i \in A, \qquad q_i = 1, \quad i \in B$$

- Find the reactive current and the effective current

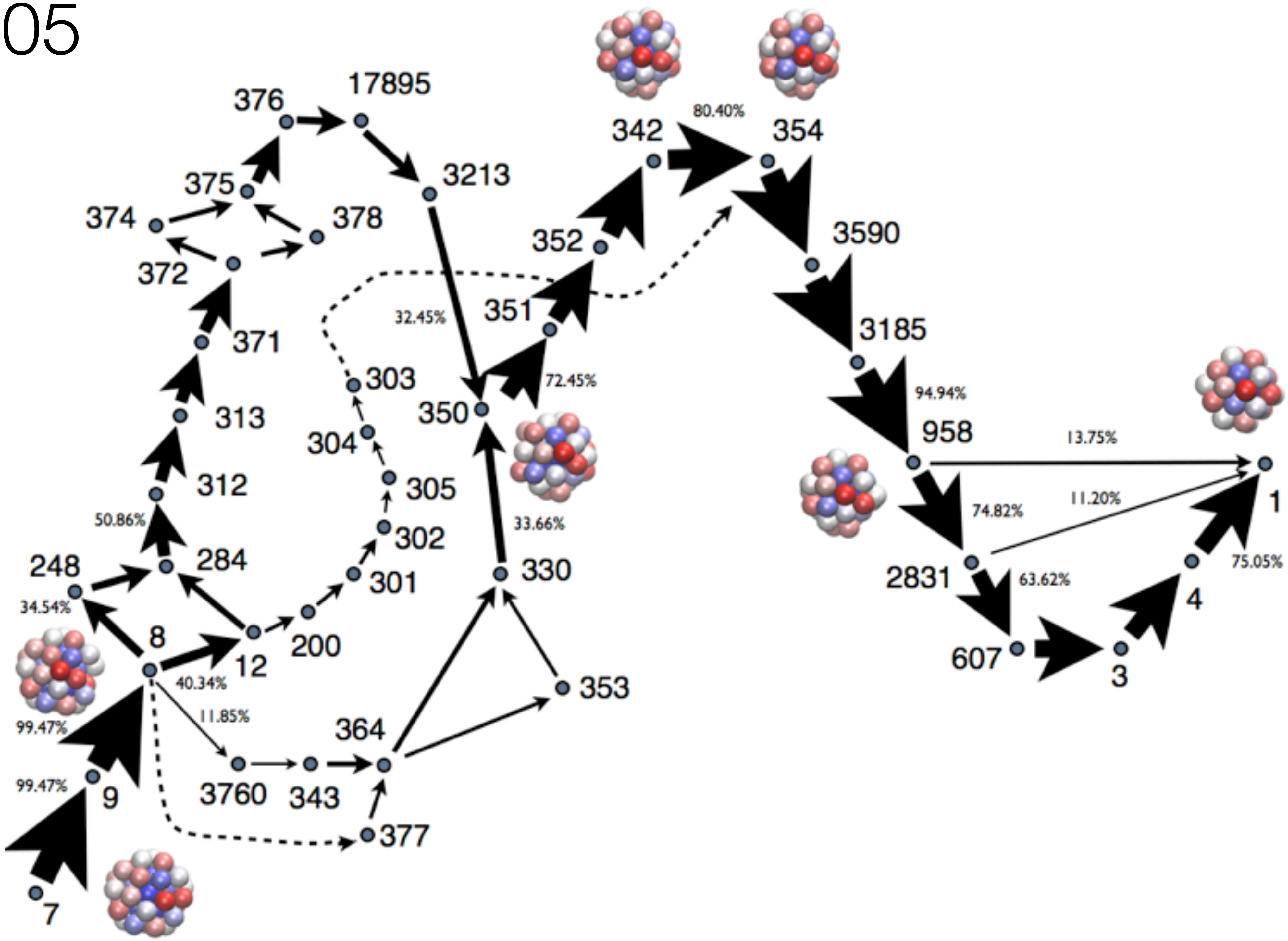
$$f_{ij}^{AB} = \begin{cases} \pi_i (1 - q_i) L_{ij} q_j, & i \neq j, \\ 0, & otherwise \end{cases} \qquad f_{ij}^{+} = \max\left\{ f_{ij}^{AB} - f_{ji}^{AB}, 0 \right\} = \begin{cases} \pi_i L_{ij} (q_j - q_i), & q_j > q_i, \\ 0, & otherwise \end{cases}$$

- Generate the reaction pathways

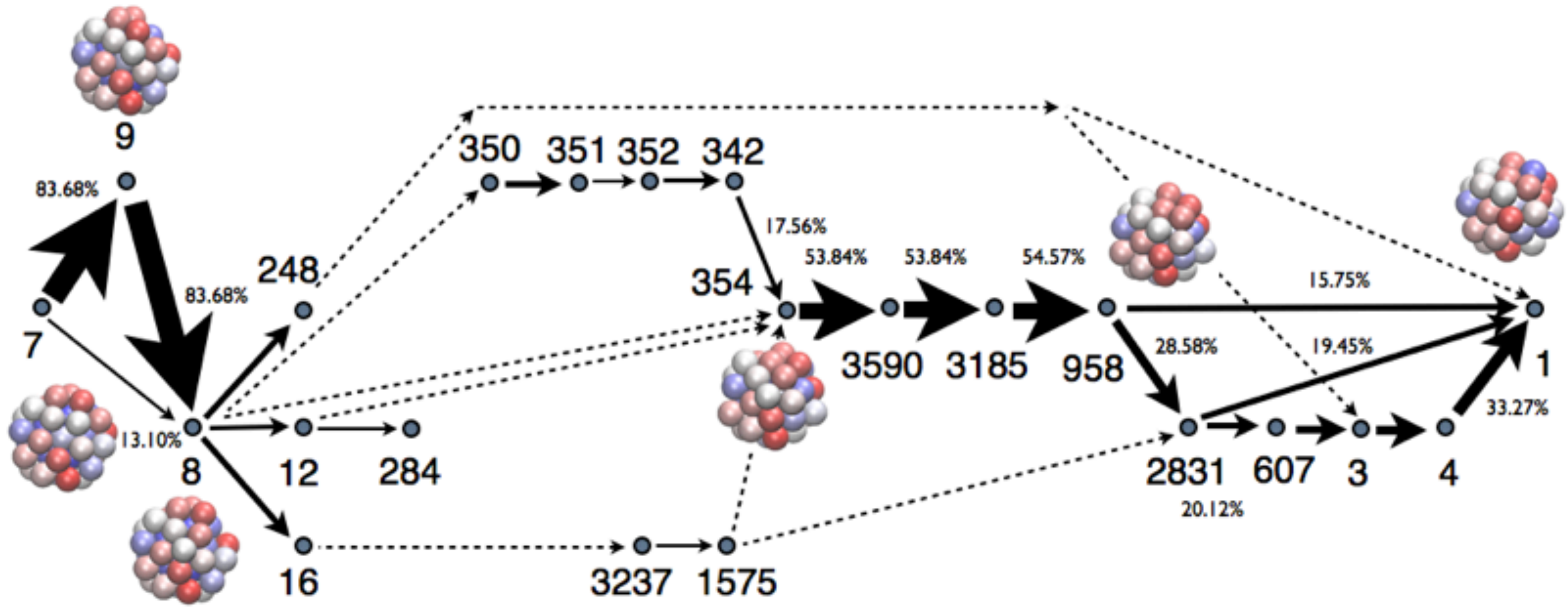
- Do statistical analysis of the reaction pathways

Transition Pathways

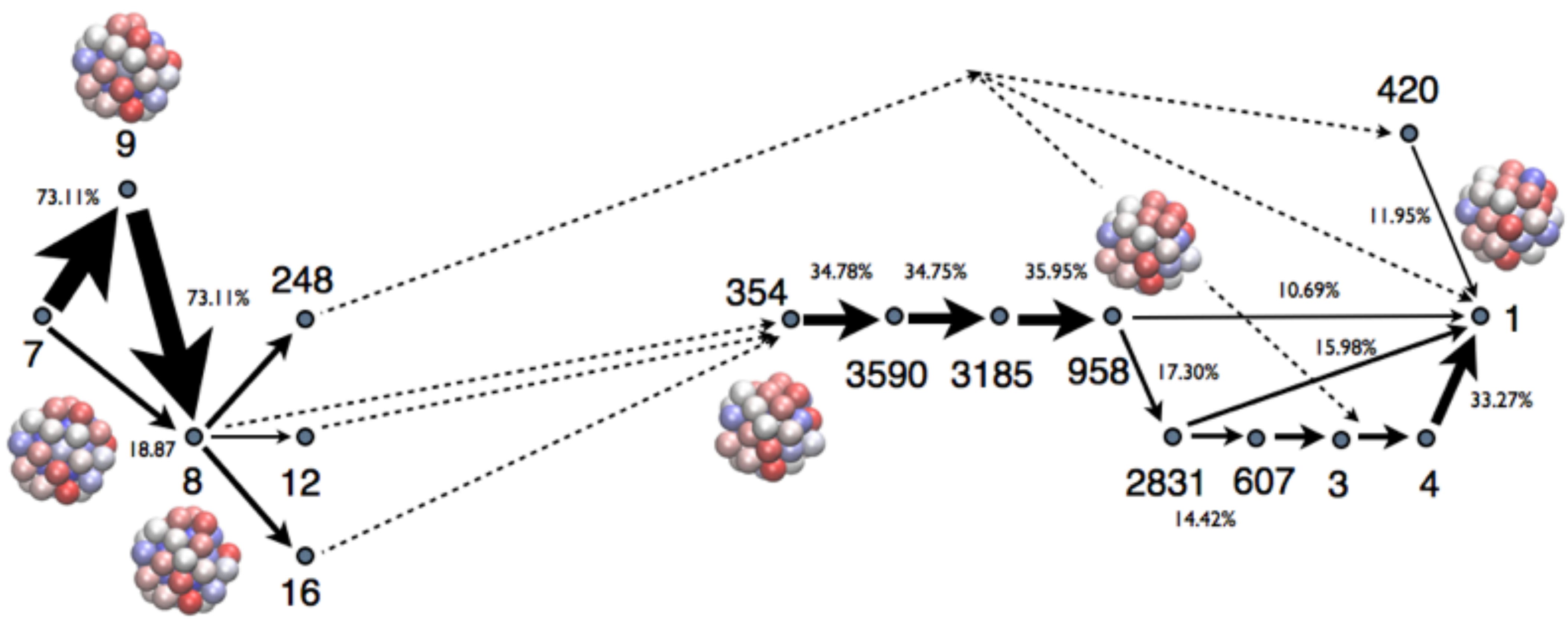
T=0.05



T=0.12

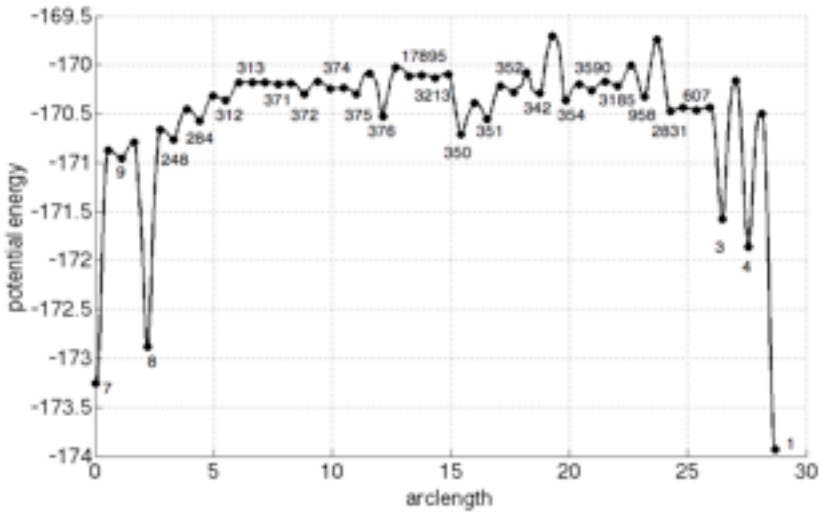

9
83.68%
83.68%
7
13.10%
8
248
12
284
16
350
351
352
342
17.56%
354
53.84%
53.84%
54.57%
3590
3185
958
15.75%
28.58%
19.45%
1
33.27%
2831
607
3
4
20.12%
3237
1575

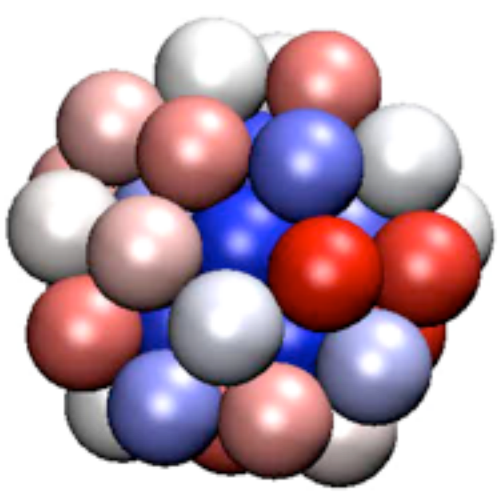
T=0.15


9
73.11%
73.11%
7
18.87
8
248
12
16
354
34.78%
34.75%
35.95%
3590
3185
958
420
11.95%
10.69%
1
15.98%
17.30%
33.27%
2831
607
3
4
14.42%

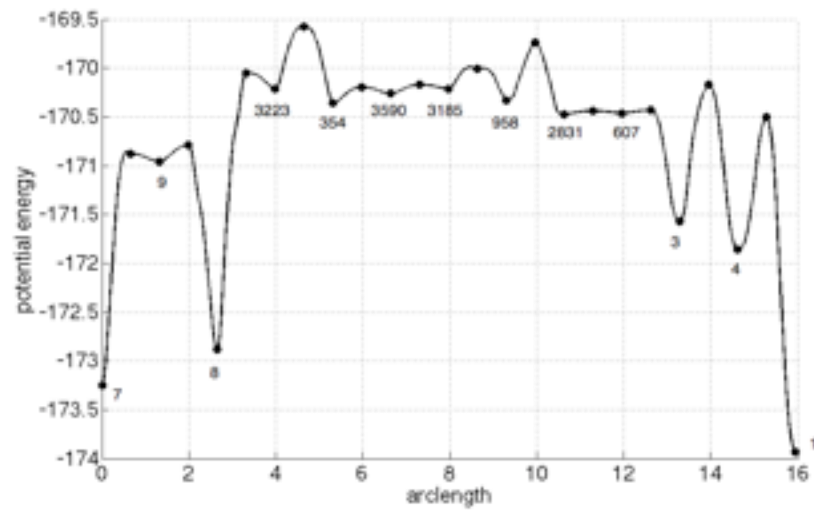
The dominant representative pathways

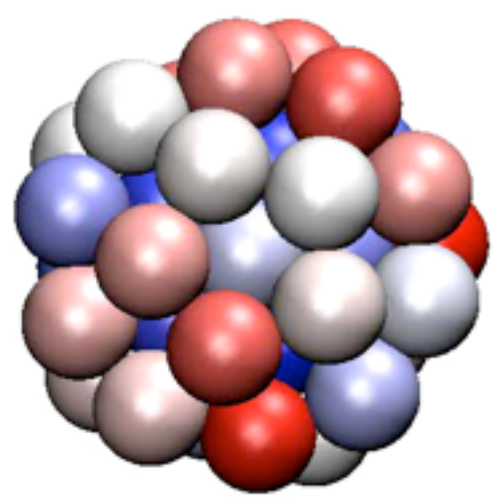
T=0.05



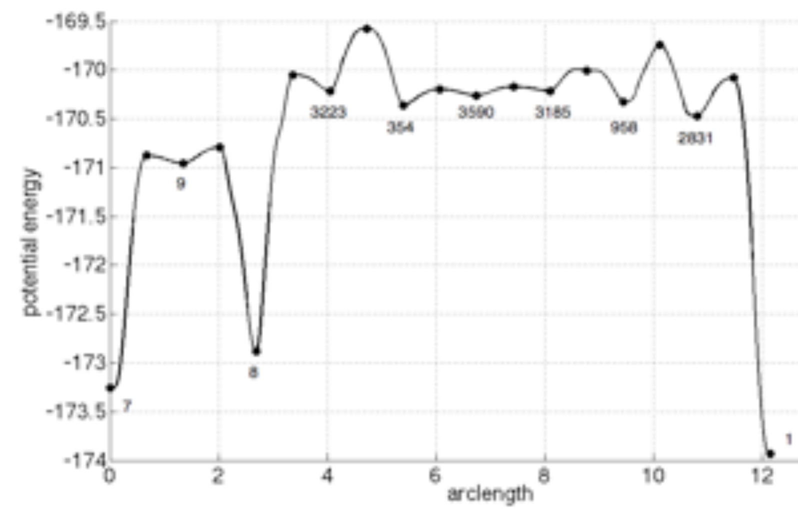


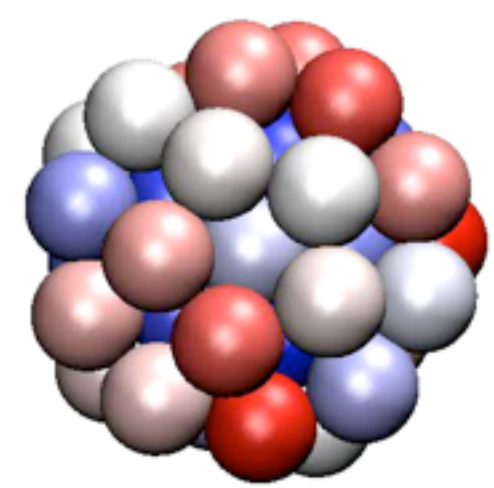
T=0.12



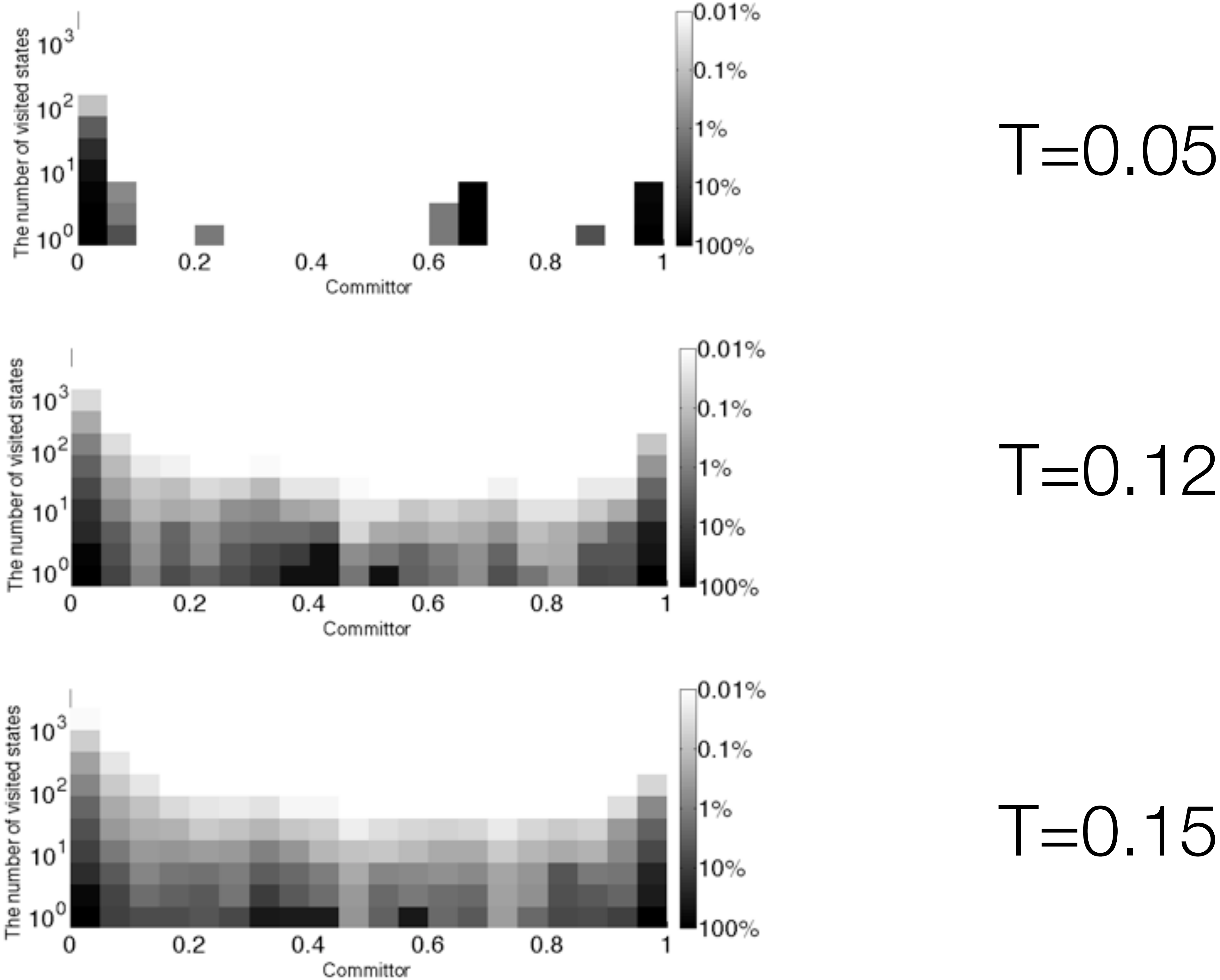


T=0.15

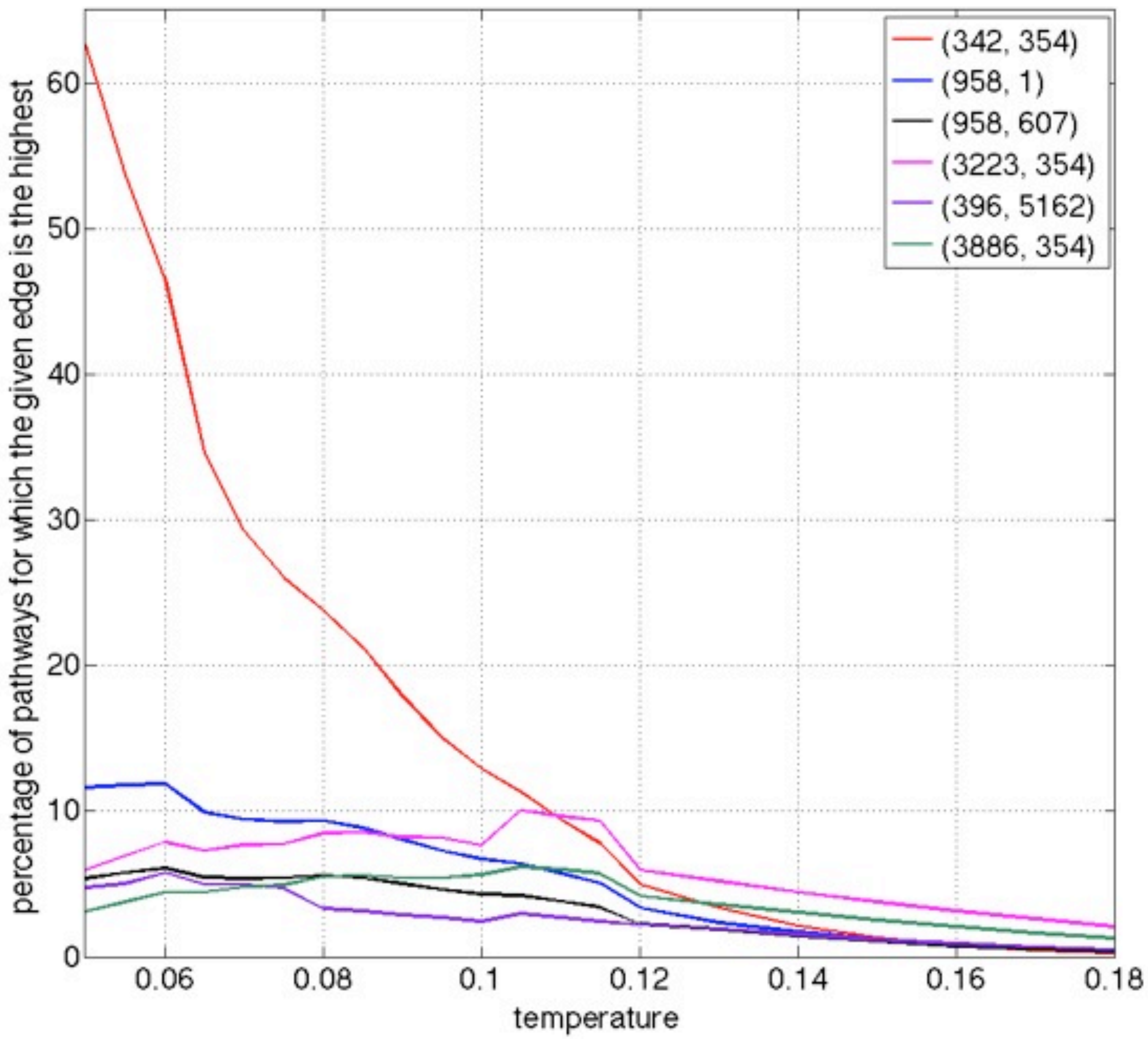




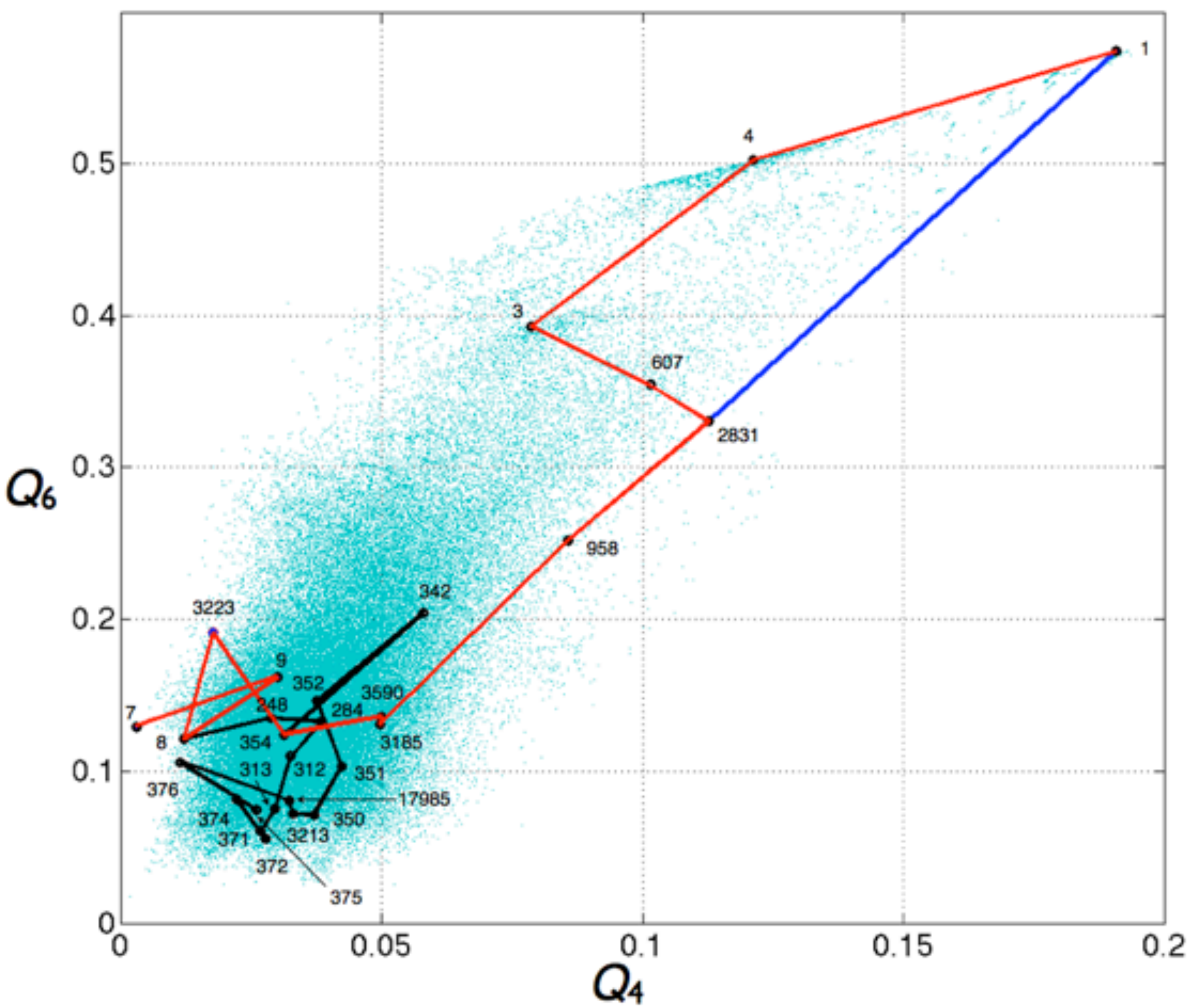
The width of the the reactive tube



The most common highest saddles



Bond-orientational order parameters



$$Q_l = \left[\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \left\langle Y_{lm}(\theta(r), \phi(r)) \right\rangle \right|^2 \right]^{1/2}$$

Y_{lm}'s are spherical harmonics, the average is taken over all bonds in cluster

A heuristic approach

$$E(w) = \sum_{(i,j)\in w} e^{V_{ij}/T}$$ - the total cost along a pathway w

$$u(i) = \min_{w} E(w)$$ - the value function is the minimum cost to get from A to i

Analogy with electric circuits

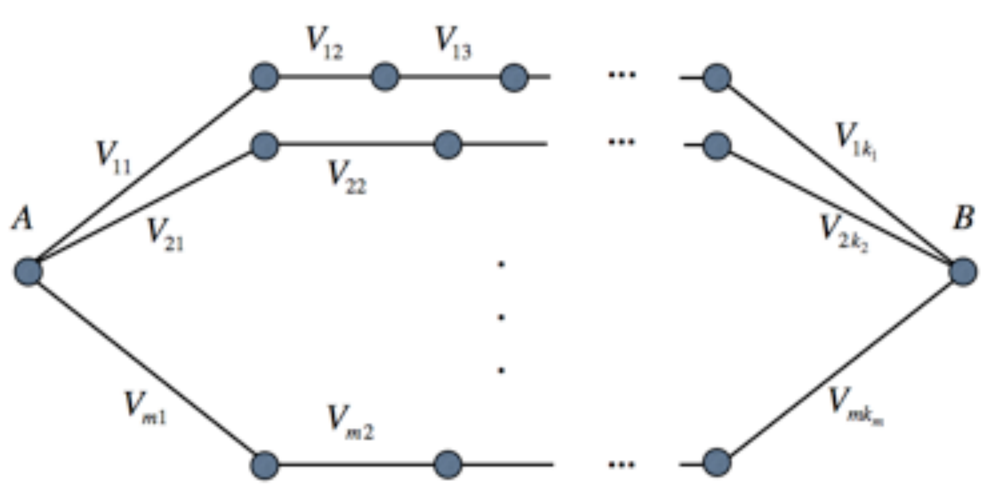
Resistance $R_{ij} = \pi_i L_{ij} = e^{V_{ij}/T}$

Electric current $I_{ij} = f_{ij}^{+}$

Electric potential $\varphi_i = 1 - q_i$

Two cases where the heuristic approach is exact

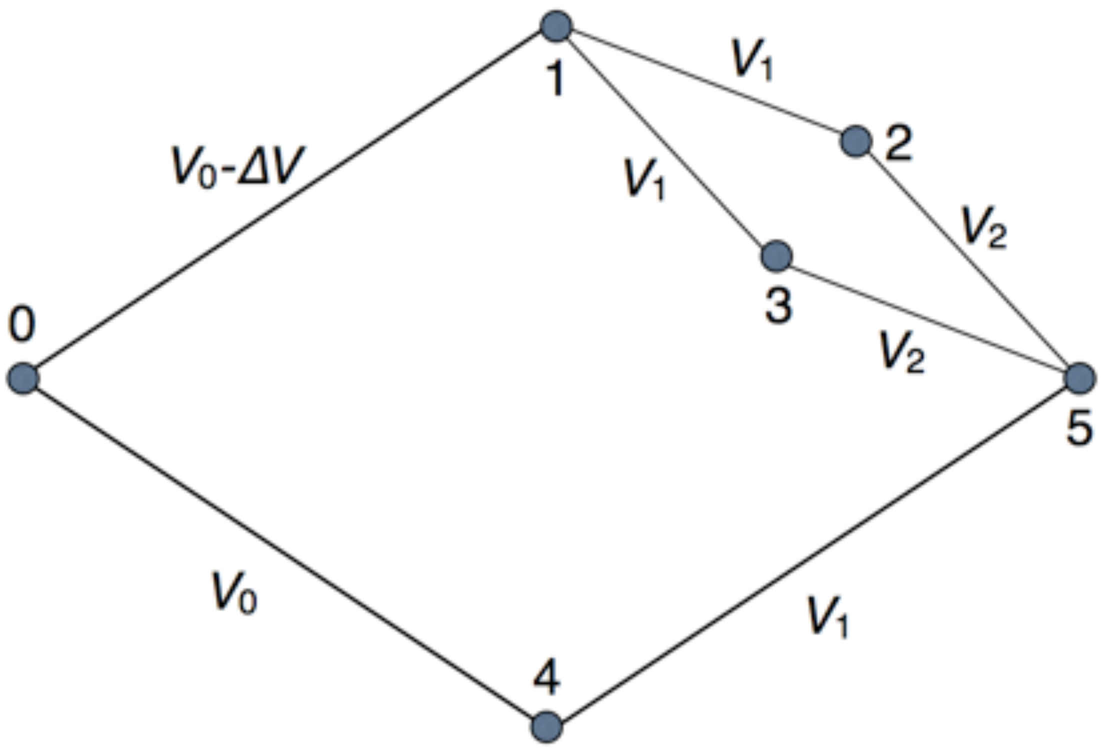
(1)



(2)

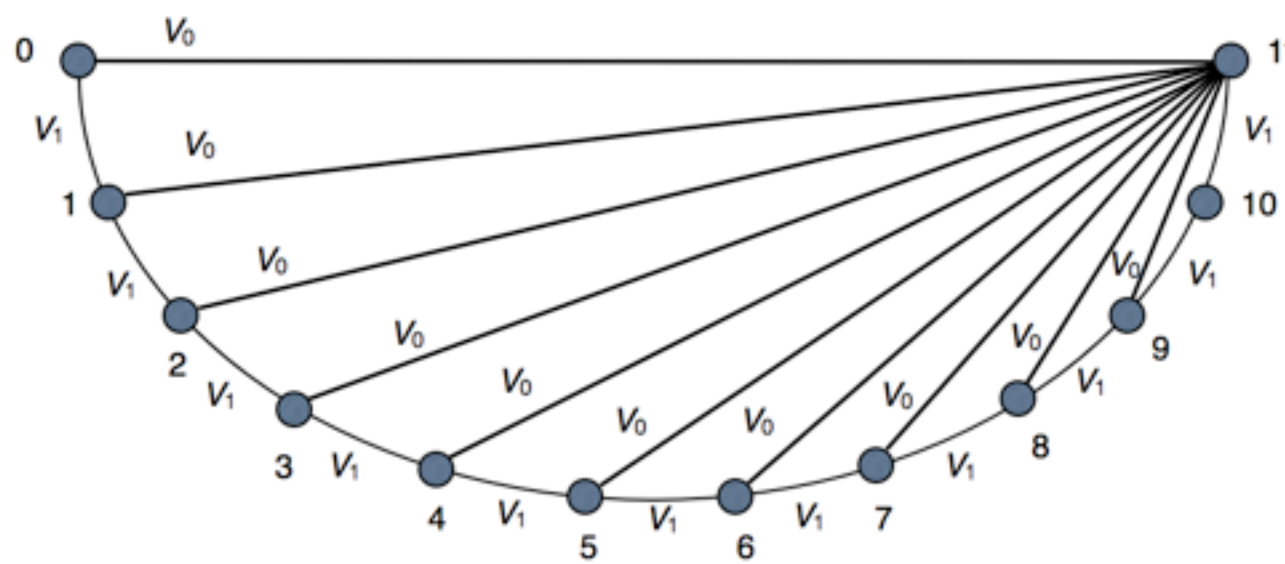
T is close to 0

The dominant representative pathways vs the minimum resistance pathways



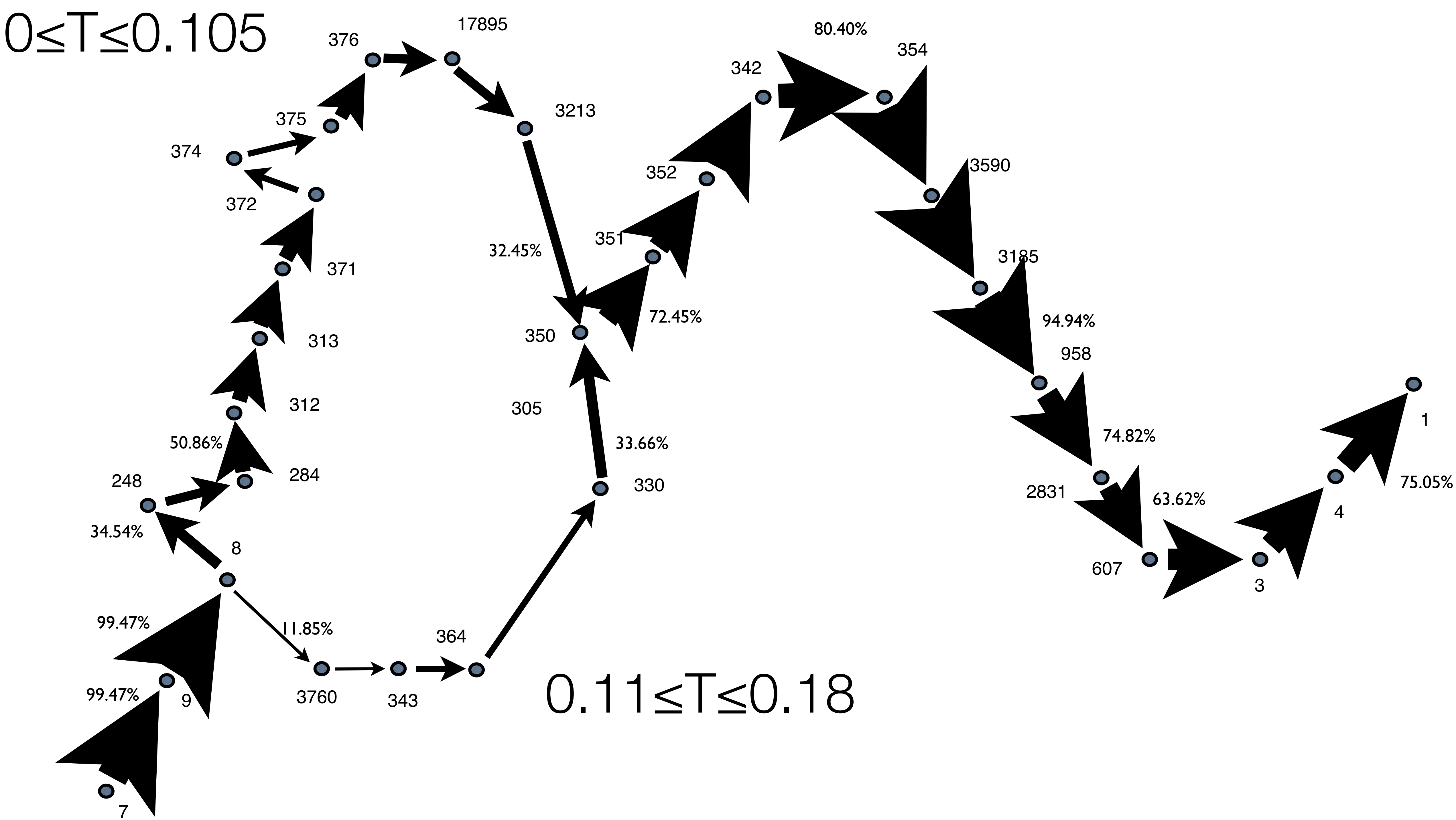
$V_0=4$, $V_1=3$, $V_2=1$, $T=1$

The dominant representative pathway:
<0,4,5>
The minimum resistance pathways:
<0,1,2,5> and <0,1,3,5>



$V_0=5$, $V_1=2$, $T=1$
The dominant representative pathway:
<0,11>
The minimum resistance pathway:
<0,1,2,3,4,5,6,7,8,9,10,11>

Minimum resistance pathways



Conclusions

- Fast and robust algorithm for computing the zero-temperature asymptotic pathway and building the hierarchy of Freidlin's cycles
- The zero temperature approach is good only for low temperatures $T \leq 0.065$, where the dominant representative pathway switches from the lowest possible highest saddle (342,354), $V=4.219$, to the higher saddle (3223,354), $V=4.352$. At $T=0.065$, the barrier (342,354) is 65 $k_B T$.
- At $T=0.12$, where the solid-solid transition occurs, the zero-temperature approach is no longer applicable. The transitions between ICO and FCC are still rare events, the barrier is 35 $k_B T$, but the temperature effects are significant.
- The heuristic approach at a given temperature tends to give an important pathway at for a lower temperature.